Pyrethroid Insecticides: Analysis, Occurrence and Fate in the Sacramento and San Joaquin Rivers and Delta

US Geological Survey
California Department of Fish and Game
California Department of Pesticide Regulation

project funded by CALFED Ecosystem Restoration Program

TAC Meeting February 14, 2007



Proposal and Funding

- Analytical method development
- •Develop, test and validate methods for analysis of 6 or more pyrethroids insecticides in water, colloids, sediments, and biota.
- Contract with USGS completed in early 2004 with subsequent subcontracts to CDFG and CDPR



Approach

LABORATORIES:

US Geological Survey
California Dept of Fish and Game
California Dept of Food and Agriculture

MATRICES:

Water: all 3 labs

Sediments:

Bed sediments – CDFG, USGS, CDFA

Suspended sediments - USGS

Colloids: USGS

Biota: CDFG



Scope of Work

Task 1: Project Management and Administration

Task 2: Project Design and Oversight

formation of TAC and annual meetings public meeting near completion of method development study design (literature review and method validation process)

Task 3: Analytical Method Development and Validation

development of analytical methods sample collection and preservation methods validation of analytical methods

Task 4: Draft and Final Report



Current Timeline for Deliverables

Contract signed with USGS on January 5, 2004 but subcontracts with CDFG and CDPR delayed until late 2004 CALFED approved a one-year no cost extension

Annual TAC meeting April 2005, March 2006,

February 2007, September 2007?

Public meeting April, 2007

Analytical methods validated July 1, 2007

Draft final report Oct 1, 2007

Final report Dec 31, 2007

Project ends Jan 1, 2008



Responsibilities of the TAC

- Participate in annual meetings
- Input on priorities from regulatory and toxicological viewpoints
- Review draft final report
- Suggestions for field studies with validated method



Agenda for Meeting

- Project Update
- Method Summary
- Inter-lab calibrations
- Public Meeting
- Final Report



Update of Method Development

Pyrethroid	CDFA	CDFG	USGS
Bifenthrin	Х	Χ	Х
Cyfluthrin (beta)	X	X	X
Cyhalothrin (lambda and gamma)	X	X	Х
Cypermethrin (alpha, beta, theta, zeta)	X	X	Х
Esfenvalerate/fenvalerate	X	X	X
Permethrin (cis and trans)	X	X	X
Deltamethrin	X	Χ	Х
Fenpropathrin	X	X	X
tau-Fluvalinate			X
Resmethrin	X	X	X
Sumithrin			X
Allethrin		X	X
Tetramethrin		X	X

Update on Method Development

Lab	Medium	Extraction Method	Volume	Analysis Method	MDLs
USGS	Water	Filtered sample; HLB cartridge with bottle rinse	1 L	GC/MS	2-5 ng/L
	Sediment (bed and suspended)	MASE/Carbon Alumina/GPC	5 g (dry weight)	GC/MS	1-5 ng/g
	Colloids	SPME	In progress		
CDFG	Water	Whole water; liq/liq extraction	1 L	GC-ECD & GC/MS	1-5 ng/L
	Sediment (bed)	ASE/GPC/ Florisil	5 g (dry weight)	GC-ECD & GC/MS	1-4 ng/g
	Tissue	ASE/GPC/ Florisil	10 g (fresh weight)	GC-ECD & GC/MS	1-5 ng/g estimated
CDFA	Water	Whole water; liq/liq extraction, florisil clean-up	1L	GC/MS & GC-ECD	1- 8 ng/L (MRL 5-15 ng/L)
	Sediment (bed)	Solvent shake, florisil clean-up	20 g (wet weight)	GC/MS & GC-ECD	0.1 – 0.9 ng/g (MRL 1-1.5 ng/g)

Water and Sediment Methods

- Optimized for equipment and instrumentation available
- Lower detection limits can only be achieved with more sensitive instruments or larger samples
 - DFG will present data from triple-quad MS
 - Larger samples not feasible for some samples (suspended sediments), also increases matrix

Method Development Questions

Sorption of pyrethroids onto containers

Addressed for most laboratory analytical purposes (bottle rinse)

USGS received additional money from EPA for field sampling SOP

Stability in solvents for calibration standards

Tested with multiple sets over several months

<10% change over six months

Water and sediment sample stability (following slides)

Include costs per sample CDFG and CDFA

Website for dissemination of data http://www.cdpr.ca.gov/docs/sw/swpyreth.htm

Environmental fate reviews (bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, permethrin)
http://www.cdpr.ca.gov/docs/empm/pubs/envfate.htm

Pyrethroid Stability in Water

- CDFA- spikes in sediment water
 - Liquid:liquid extraction with Florisil clean-up
 - Spike
 - 87-100% recovery at 0 days
 - 50-100% recovery at 4 days
 - 50-90% recovery at 7 days
 - Keeper solvent (10 mL hexane)
 - 95-100% recovery at 0 days
 - 65-100% recovery at 4 days (most compounds better than before keeper)
- USGS SPE Cartridges
 - Pyrethroids are stable for 28 days on HLB cartridge (frozen)
- Need to analyze water samples quickly, within 24 hours is optimal

Pyrethroid Stability in Sediment

- CDFA- pyrethroid spikes onto sediment
 - Stable for one month
- USGS Analysis of sediment
 - Extracted after collection and after one year
 - Lamda-cyhalothrin concentrations were the same

Pyrethroid Inter-Lab Comparisons Water

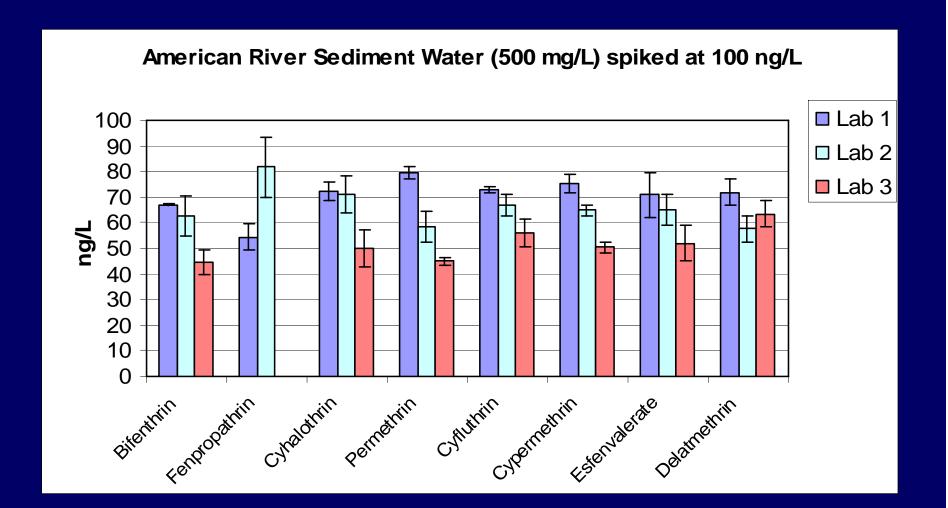
- Spiked American River water (with 500 mg/L CBD sediment) and CBD water (6 mg/L DOC; 14 mg/L suspended sediment)
- Samples spiked in 20 L soda kegs
- With continuous stirring, water was pumped into 1 L glass bottles
- 2 concentrations: 10 ng/L and 100 ng/L
- Each lab received samples and spiking solution (2 ng/mL)
- Samples extracted within 48 hours (2 used liquid:liquid and one used SPE + filter extract)
- GC-ECD and MS detection
- No detects in blanks for any of the labs

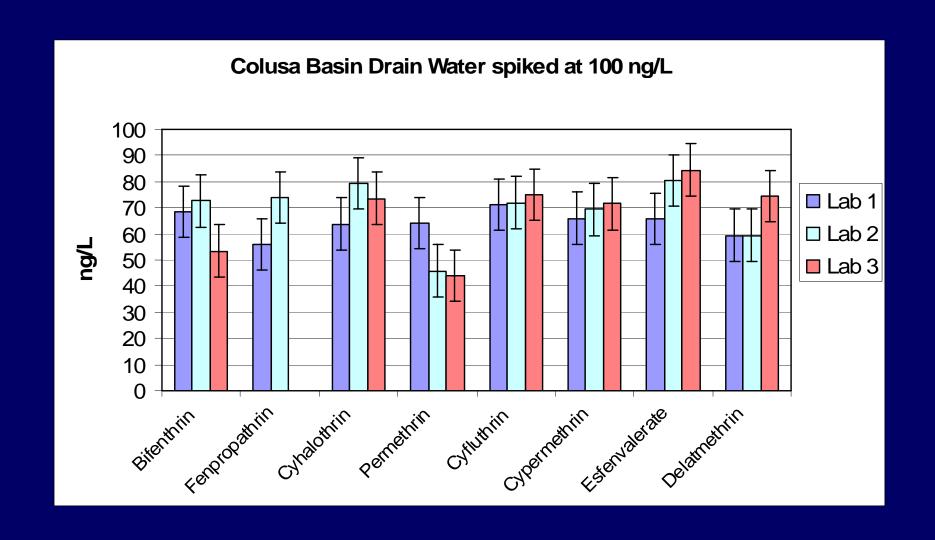
Spiking Solution

- Sent out spiking solution (used by USGS) to labs
- Agreed on concentration of spike (± 10%)

Low Level Water Samples (10 ng/L)

- 10 ng/L
- One lab: below MRL
- Lab # 1 ~3-9 ng/L
- Lab # 2 ~ 3-8 ng/L



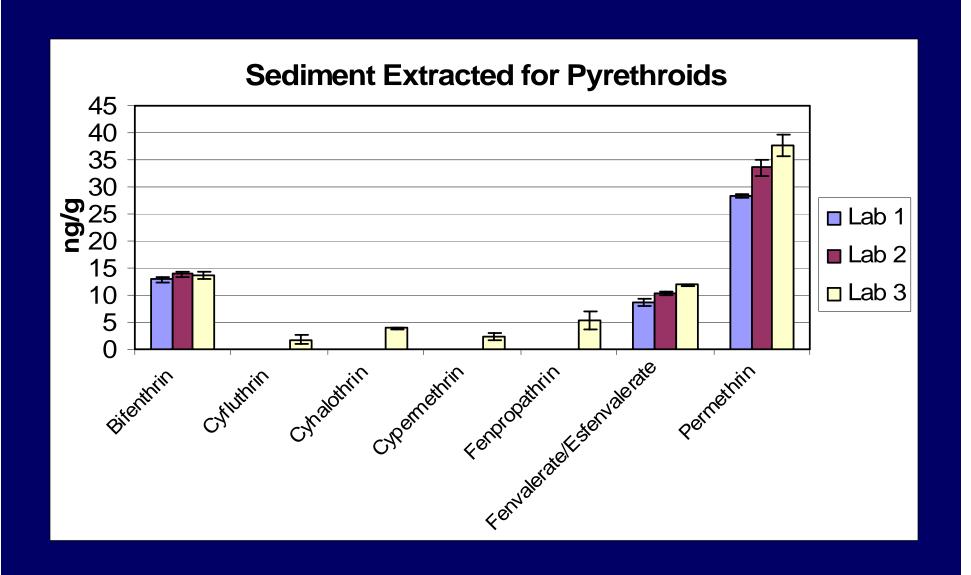


Pyrethroid Water Summary

- 10 ng/L did not work well, too low with 500 mg/L sediment
- Sediment water (500 mg/L),
 - Highest suspended sediment concentration
 - Fairly good agreement but concentrations measured were lower than expected (50-70%)
- Colusa Basin Drain
 - Better recovery (>70%) and all concentrations with one standard deviation
 - Composition more similar to most waters sampled

Pyrethroid Inter-Lab Comparisons Sediment

- Sediment collected from Salinas area by DPR
- All labs received 2 1-L jars of sediment
- Extractions were completed within one month
- One lab used shaking, one microwave and one pressurized solvent extraction



Pyrethroid Inter-Lab Comparisons Sediment

- Slight differences in concentrations due to extraction methods
- Sonication has been shown the quantify 30% less than heated or pressurized extractions for OC and OP pesticides on aged sediments
- Also retain less matrix

Public Meeting

- Must be held in April
- Room reserved at Cal EPA for April 25th 9 am –
 1pm
 - Change location?
- Topics to cover
 - Methods
 - Water and Sediment
 - Advantages and Disadvantages
 - Validation (inter-lab calibrations)
- Groups to Invite

Final Report

- Validated methods must be given to CALFED by July 1
 - Include full methods
 - Recoveries
 - MDLs
 - Include inter-lab calibrations
- Final Report
 - No desired format
 - Stability, sorption